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Dr. Thomas Somcynsky left the University at the end of the summer to assume an academic position in Canada. The research is being carried out currently by Dr. R. A. Haldon, and two Ph.D candidates, Mr. Philip Rawlings and Mr. William Schell.

#### 1. MULTIPLE TRANSITIONS IN VARIOUS POLYMER SYSTEMS

A series of polyalkyl methacrylates has been studied by both length - temperature and low frequency dynamic mechanical measurements, from liquid nitrogen temperatures to above the respective glass temperature. The two techniques have allowed a comparison of results. The polymers studied include the n-alkyl homologues from methyl to butyl, the other three isomers of butyl, hydroxy ethyl, hydroxy propyl and methoxy ethyl methacrylates and polymethyl acrylate. The flexible side chain samples exhibit two  $T_{gg}$  transitions in the temperature range  $T_g - 100 < T_{gg} < T_g$ , and the ones with bulky side groups, i.e. methyl and t-butyl, only one. The lower transition is probably associated with rotation of the carbo-alkoxy side group, and the upper one, characteristic of the flexible side chains, may be a crankshaft motion of about one monomeric unit about the chain axis. Analogous to  $T_g$ , both  $T_{gg}$  transitions are affected by side chain geometry, moving to lower temperatures on lengthening the side chain, and to higher temperatures within the butyl isomer series. The hydroxy polymers have transition temperatures higher than the corresponding alkyl polymers, due to inter-chain hydrogen bonding. This property also gives expansion coefficients about one half as large as those for the alkyl systems.

A third transition found about  $-120$  to  $-80^\circ\text{C}$  may be associated with adsorbed water molecules. There is evidence, in the n-alkyl series, of a fourth transition located about the lower limit of our temperature range. This would be consistent with the  $-150^\circ\text{C}$   $\gamma$ -transition found for a similar series, by a

high frequency technique. This probable transition will be better characterized in the near future by our measurements at liquid helium temperatures.

It has been previously demonstrated that the Simha-Boyer free volume product,  $(\alpha_l - \alpha_g) \cdot T_g$ , decreases with increasing side chain length for this series, due to side chain motion retaining excess free volume below  $T_g$ . However for all polymers, except those with interchain hydrogen bonds and poly t-butyl methacrylate, substitution of  $\alpha'_{g''}$ , the expansion coefficient below our  $T_{gg}$  (2) transition, gave a value of about 0.11, close to that observed for linear polymers.

The L-T data has been compared with the results obtained with a torsion pendulum at a frequency of about 1 Hz.  $T_g$  obtained by the latter is higher than that obtained by dilatometry, consistent with the higher frequency of the dynamic technique. One very broad secondary peak was observed, spanning the temperature range of the two LVDT  $T_{gg}$  transitions, and tending to merge with  $T_g$  on increasing the alkyl side chain length. It appears then that better resolution is obtained by the dilatometric technique. A manuscript on this polymer series is in preparation, and the work is shortly being extended to cryogenic temperatures, and longer n-alkyl side chains.

A similar series of polyvinyl n-alkyl ether elastomers was studied in the temperature range  $-180^\circ\text{C}$  to room temperature. Length-temperature measurements with the LVDT apparatus on polyvinyl methyl, ethyl and n-butyl ethers have shown that the free volume at  $T_g$  defined by the Simha-Boyer equation decreases with increasing side chain length. The high values of  $\alpha_g$  obtained are indicative of retained free volume by motion of the flexible side chains below  $T_g$ . Preliminary investigations at liquid nitrogen temperatures have indicated  $T_{gg}$  transitions in the polymers having a side chain longer than methyl ether. The data suggest that there are  $T_{gg}$  transitions below our working temperature. These will be studied in the future at liquid helium temperatures. Further work is

in progress measuring the expansion coefficients and transitions of the higher alkyl side group polymers.

The differential scanning calorimeter was used to determine the heat capacity  $C_p$ ,  $T_g$  and  $\Delta C_p$  at  $T_g$  of these polymers, up to a side chain length of 18 carbon atoms. The data indicate that  $\Delta C_p$  in cal/mole of beads (as defined by Wunderlich) for the methyl and ethyl ether side chain containing polymers is constant and is within the range of the empirical value of  $2.7 \pm 0.5$  cal/mole. For the higher alkyl side group polymers,  $\Delta C_p$  increases as the length of the side chain increases, presumably due to a breakdown of the simple bead theory. The glass transition of this series decreases with increasing side chain length, due to increased segmental mobility, to a minimum of  $-71^\circ\text{C}$  for polyvinyl n-octyl ether. Thereafter  $T_g$  increases. It was noted that side chain crystallization was present above polyvinyl n-octyl ether, and this will explain the increase in  $T_g$ . In the poly n-alkyl methacrylate series, side chain crystallization first occurs in poly n-hexadecyl methacrylate corresponding also to the minimum  $T_g$  in that series. This difference between these series is due to the bulkier and more polar structure in the alkyl methacrylates.

Three polyethylene terephthalates have been studied by both the length - temperature technique and by differential scanning calorimetry. Crystallinities were determined from the observed heats of fusion, using the heat of fusion for a 100% crystalline sample proposed by Dole, as a standard.

Two samples of very low crystallinity have expansion coefficients that compare favorably with the literature, and both exhibit two  $T_{gs}$  transitions at about  $-87^\circ\text{C}$  and  $-15^\circ\text{C}$ . The literature presents evidence for only one high frequency dynamic loss peak about  $-40^\circ\text{C}$ . Increasing the crystallinity of one sample gave lower expansion coefficients and moved the main glass temperature from about  $65^\circ\text{C}$  to about  $85^\circ\text{C}$  with evidence of a distribution of glass tempera-

tures. Both  $T_{gg}$  transitions persisted although the upper may have moved to lower temperatures. The third sample, of higher crystallinity, had a very low coefficient of expansion at low temperatures, much lower than that expected from the literature data.

Scanning calorimetry indicated that both samples of low crystallinity underwent a "cold crystallization" at about 140°C. The amount of "cold crystallized" polymer which could be obtained was a constant, approximately 35%. This indicates that about 65% of the polymer is involved in twist points. Samples annealed to greater than 35% crystallinity exhibited no "cold crystallization" exotherm, and the glass temperature was difficult to observe. Preliminary studies indicated that whilst  $T_g$  and the location of the cold crystallization exotherm were heavily dependent on the rate of heating,  $T_m$  was virtually independent of it.

Further characterization of the samples is being obtained and further work is in progress.

We are examining, in co-operation with Dr. L. Utracki, the relationship between diluent concentration and the main glass temperature,  $T_g$ , for the systems polystyrene-diethyl phthalate and polystyrene-dibenzyl ether. At present, this is a preliminary examination, utilizing the differential scanning calorimeter, to check the technique and to compare the results with published data. In addition to being of interest per se, this dependence should play a role in determining the dependence of melt viscosity and high concentration solution viscosity on concentration, a problem we are investigating in another research effort.

## 2. EQUATION OF STATE PROPERTIES

In the last report we described a hole theory applied to both polymer and monomer liquids. An important quantity in this theory is the number of holes in the system derived for thermodynamic equilibrium as a function of temperature and volume by a minimization of the configurational free energy. We have now applied this theory to glasses and explored the consequences of the assumption that at  $T_g$  this number is frozen in and remains constant. We find that the product  $\alpha_g T_g$  is nearly independent of the reduced volume,  $\tilde{V}$ , and smaller than is experimentally observed. The predicted Simha-Boyer product  $(\alpha_l - \alpha_g) \cdot T_g$  varies markedly more than experiment indicates. This result therefore suggests that the freezing of the number of holes at  $T_g$  is too drastic an assumption.

We are exploring an alternative to the hole theory of the equation of state properties, which is based on the concept of a nearest neighbor distribution around a given molecule, as developed by Bernal on purely geometric grounds and given a statistical mechanical formulation by Fürth. As in our earlier work the position of the theory is first examined for monomer fluids. A good measure of numerical computation is required to gauge the merits of this approach.

## 3. PUBLICATIONS

Some Consequences of the Gibbs-DiMarzio Theory of the Glass Transition, J. Moacanin and R. Simha, J. Chem. Phys., 45, 964 (1966).

Low-Temperature Thermal Expansivities of Polyethylene, Polypropylene, Mixtures of Polyethylene and Polypropylene, and Polystyrene, J. L. Zakin, R. Simha and H. C. Hershey, J. Appl. Polymer Sci., 10, 1455 (1966).